

# Application of Glow Discharge Plasma to Alter Surface Properties of Materials

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**Abstract**—Some polymer materials that are considered important for spaceport operations are rendered noncompliant when subjected to the Kennedy Space Center (KSC) Standard electrostatic testing. These materials operate in stringent environmental conditions, such as high humidity. Treating materials that fail electrostatic testing and altering their surface properties so that they become compliant would result in considerable cost savings. Significant improvement in electrostatic dissipation of Saf-T-Vu PVC after treatment with air Atmospheric Plasma Glow Discharge (APGD) was observed and the material now passed the KSC electrostatic test. The O:C ratio on the surface, as monitored by X-ray Photoelectron Spectroscopy, increased from 0.165 to 0.275 indicating enhanced oxidation, and surface contact angle measurements decreased from 107.5° to 72.6° showing increased hydrophilicity that accounted for the increased conductivity. Monitoring of the aging showed that the materials hydrophobic recovery resulted in it failing the electrostatic test 30 hours after treatment. This was probably due to the out-diffusion of the added Zn, Ba, and Cd salt stabilizers detected on the surface and/or diffusion of low molecular weight oligomers. On going work includes improving the long term hydrophilicity by optimizing the APGD process with different gas mixtures. Treatment of other spaceport materials is also presented.

## I. INTRODUCTION

There are several polymer materials considered important for spaceport operations. These materials operate in stringent environmental conditions, where it is critical that any charge build-up on the surface of the materials be dissipated as quickly as possible. All materials considered for use in spaceport operations are subjected to the Kennedy Space Center (KSC) standard electrostatic testing [1]. In this test, the materials are rubbed for 10 seconds against PTFE or wool at  $45 \pm 3$  % relative humidity (RH), and the charge decay measured as a function of time. To pass the test, the charge on the materials must decay to below 350 V in less than 5 seconds. Several materials have failed the test but are considered favorable for use in Space Shuttle, International Space Station, and Launch Services Programs. These polymeric materials have excellent bulk and physical properties, are easy to process, and are relatively inexpensive. It is often required to have certain surface properties that the bulk material does not possess, such as hydrophilicity, roughness, and conductivity. Therefore, it is necessary to modify the surface of a polymer, without affecting the bulk property. Treating materials that fail electrostatic testing and altering their surface properties so that they become compliant would result in considerable cost savings and improve safety. The goal of this project is to use Atmospheric Plasma Glow Discharge (APGD) to alter the surface properties of polymers for improved electrostatic dissipation characteristics.

Many advances have been made in developing surface treatments, including plasma, corona, photons, electrons, flame, ion beams, and X-rays [2, 3]. These treatments can produce special functional groups at the surface, increase the surface energy, increase or decrease hydrophilicity, improve chemical inertness, introduce cross-linking, remove weak boundary layers and contamination, and increase the surface morphology. The advantage of an APGD is that it can be used in atmosphere eliminating the need for an expensive vacuum chamber, and also operates at low temperatures, minimizing heat damage to the polymer surface. Oxygen and oxygen-containing plasmas are the most commonly used. An APGD using  $O_2$  or air creates free radicals (N, O, OH...) and excited species ( $N^*$ ,  $N_2^*$ ,  $O^*$ ,  $O_2^*$ ...) that form active products ( $O_3$ ,  $H_2O_2$ ,  $HNO_2$  and  $HNO_3$ ) that chemically react with the surface improving the wettability. The depth of surface modification depends upon the power level and time of treatment. For polymer samples, it is typically several hundred angstroms. However, if UV is generated in the plasma, the depth of UV induced cross-linking can be greater than a micron.

After plasma treatment, the important factors that can be detrimental to the modification are the effects of aging, caused primarily by the environment and temperature. Polymer chains are more mobile on the surface than in the bulk, allowing reorientation. This may be due to diffusion of low-molecular weight oxidized material into the bulk and migration of polar functional groups.

These polar groups are in a high-energy state, and attempt to reduce the interfacial energy by migration into the bulk. High temperatures can accelerate the above processes, whereas low-temperatures have been shown to reduce the aging affect. Once a surface has been modified, the effect of the modification on the surface topography and chemistry needs to be monitored.

Several candidate films have been identified as vital by Space Shuttle ground operations that failed the electrostatic tribocharging testing for use during processing. These materials are Rastex (orbiter radiator protective covers), Frommelt Saf-T-Vu M1083 (Solid Rocket Booster joint enclosures for segment mating operations), Herculite 20 white, Herculite 20 Blue, Herculite 10W yellow, and Saf-T-Walk. Allowing the use of a wider range of materials would considerably reduce product and handling costs and provide less stringent working conditions such as operating at high relative humidities.

## II. EXPERIMENTAL

### A. Atmospheric plasma treatment

A PlasmaSol (Hoboken, NJ) atmospheric plasma head that utilizes oxygen or air was chosen for use. This instrument is still in the development stage and collaboration between NASA's Electrostatics and Surface Physics Laboratory (ESPL) and PlasmaSol is ongoing for future improvements. A schematic of the final set-up is shown in Figure 1.

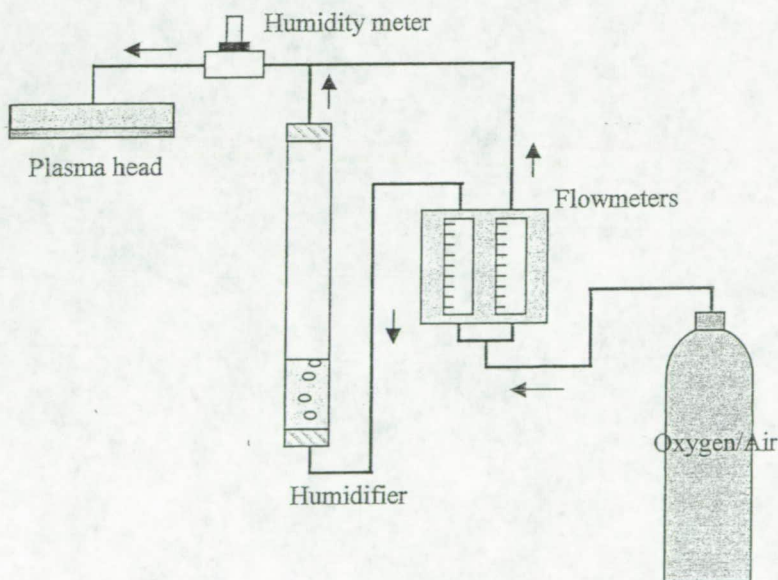


Fig. 1. Schematic of Atmospheric Plasma set-up utilizing oxygen or air.

In the set-up, a humidifier was included so that the relative humidity of the oxygen could be varied to determine if it would enhance the surface reactions. The flow rate of the gas to the head was  $5 \text{ lmin}^{-1}$  at 25 psi. The plasma is considered effective 1-5 mm from the head surface. Figure 2 shows a close-up of the plasma head and the rotating platform on which the samples were mounted to ensure even exposure to the plasma.

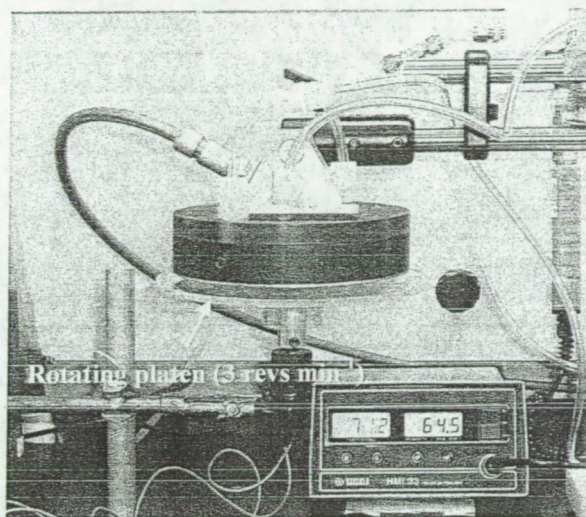


Fig.2. Close-up of plasma head and rotating platform.

Two sets of nine coupons were cut out from each material. The first set was exposed to an air plasma and the second to an  $\text{O}_2$  plasma. Previous trial runs using  $\text{O}_2$  plus water vapor had not proved effective due to the high humidity quenching the plasma and so were not included. Each coupon from each set was exposed for a set time. The times of exposure were 0, 0.5, 1, 2, 4, 8, 10, 15, and 20 minutes. The treatments were performed at  $45 \pm 3\%$  RH and at  $72^\circ\text{F}$ .

#### B. X-ray Photoelectron Spectroscopy Analysis

Coupons of each material as-received were analyzed in a Kratos XSAM800 XPS system at a base pressure of  $10^{-9}$  torr.  $\text{Mg K}\alpha$  X-rays ( $1253.6 \text{ eV}$ ) at 180W were used to analyze each surface before and after various plasma exposure times. Survey scan spectra were collected that showed the presence of all elements on the surface. The survey scans were taken from 0 -1100 eV kinetic energy at 1 eV steps with a 50 ms dwell time for 10 scans. The relative concentrations of the detected elements were calculated by measuring the area under each peak and normalizing with sensitivity factors supplied by the instrument manufacturer. XPS is a surface sensitive technique in that the escape depth of

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Images taken on the contact angle instrument of the water droplet on the surface of the Saf-T-Vu before and after plasma treatment are shown in Figure 4. The mean measured contact angle dropped from 107.5 ° to 72.6 ° indicating a significant increase in the hydrophilicity of the surface.

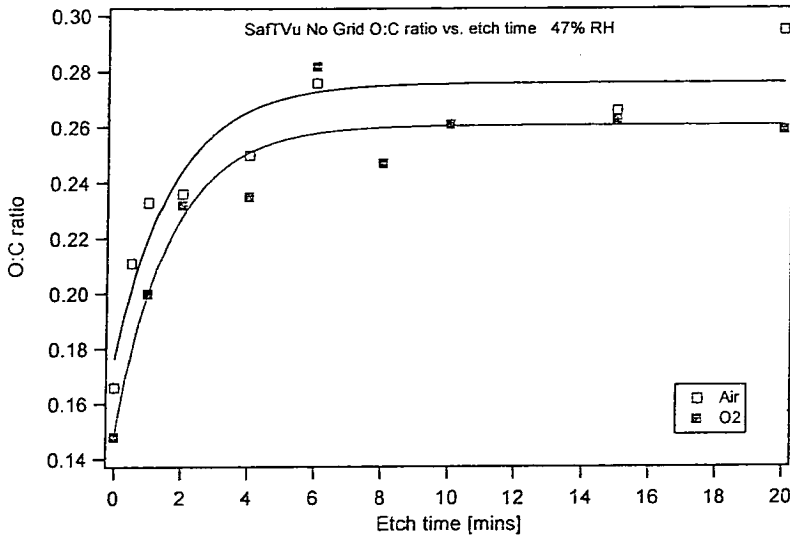


Fig. 3. Plot of the oxygen-to-carbon ratio (O:C) as determined from the XPS data as a function of plasma treatment time. Maximum effectiveness was observed after 6 – 8 minutes

TABLE 1: RELATIVE ATOMIC CONCENTRATIONS OF SAF-T-VU FROM THE XPS DATA BEFORE AND AFTER PLASMA TREATMENT

	C	O	Cl	Zn	Ba	Cd
Control	80.6	11.8	5.9	0.9	0.7	0.2
Air 6 mins	70.5	19.4	8.4	1.1	0.4	0.2

The tribocharge decay plot of the as-received Saf-T-Vu (Figure 5, plot (a)) showed the surface voltage did not meet the electrostatic acceptance criteria of 350V or less within 5 seconds after termination of charge generation at 47% RH. After plasma treatment, the material surface charged up considerably less and passed the test (plot (b)). Further tests taken in time up to 141 hours (plots (c) to (h)) after treatment showed that the surface recovered to nearly its pre-plasma treatment performance. From the plots in Figure 5, the surface voltage noted at 5 seconds after treatment was plotted as a function of aging time and



is shown in Figure 6. It was observed that the surface recovered to fail the test after about 30 hours.

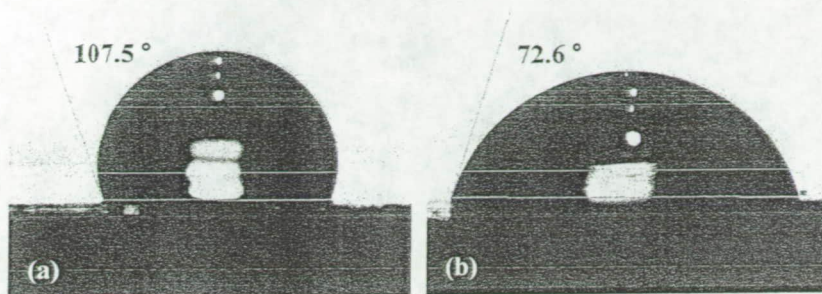


Fig. 4. (a) Contact angle of DI water on Saf-T-Vu as-received, and (b) contact angle after 6 minutes plasma treatment showing increased hydrophilicity

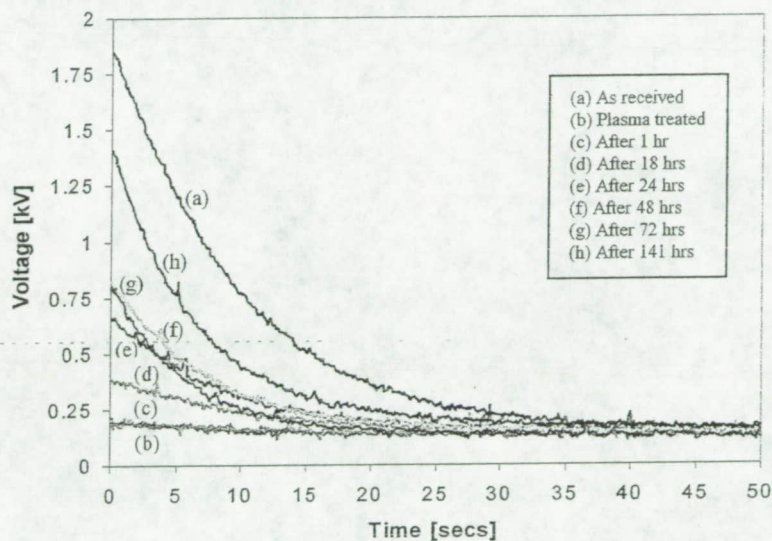


Fig. 5. Triboelectric charge decay before and after plasma treatment

The data showed that air plasma treatment increased the hydrophilicity of the Saf-T-Vu surface, resulting in a dramatic decrease in the charge accumulation due to the adsorbed moisture carrying away the surface charges. However, exposure to the environment over time resulted in this effect disappearing after about 30 hours. The hydrophobic recovery of plasma treated polymer

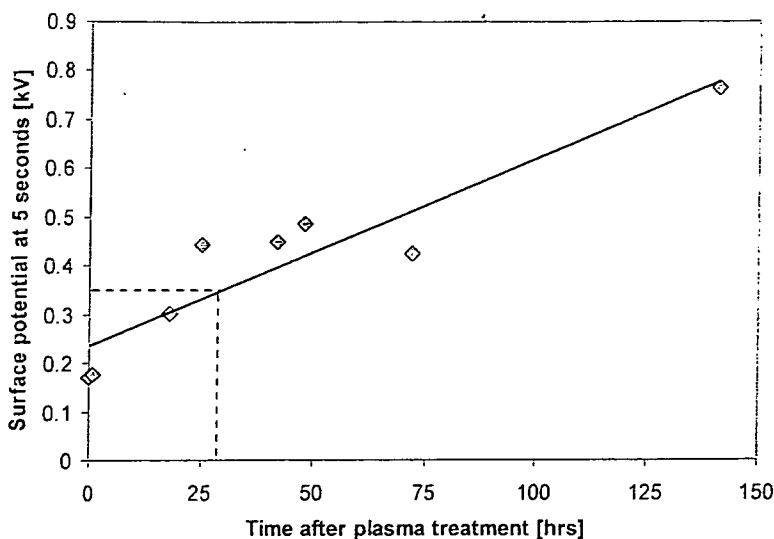


Fig. 6. Residual triboelectric charge voltage at 5 seconds after termination of charge generation as a function of aging time after plasma treatment

surfaces have been well studied [5, 6]. In general, the surfaces tend to reorient or reconstruct in response to different environments to try and minimize the interfacial energy. However, the amount of recovery depends a lot upon the plasma used and the stored environment and differs between polymers. Also the incorporation of additives can play a big part. The XPS data showed the presence of stabilizers in the Saf-T-Vu. Although not in great concentrations, they tend to be present as carboxylate complexes or stearates, and the diffusion of these additives to the surface can disrupt the stability of the surface [7].

For future work, a second plasma head that utilizes helium and oxygen has been received. It has been shown that  $\text{He} + \text{O}_2$  plasma treatment provides for more oxidation on polymers [8].

At present the aging effects of the APGD treatment are being studied on all materials. Additionally, the effects of APGD on aluminum and 316L stainless steel (two Spaceport structure materials) on the surface chemistry are also being investigated. The hydrophobic recovery of treated materials and effects on wettability will be monitored over the next several months using XPS and surface contact angle measurements to determine the long-term aging effects of any degradation of the surface modification.



#### IV. CONCLUSION

Exposure to atmospheric plasma glow discharge significantly improved the hydrophilicity of spaceport polymer materials, and resulted in Frommelt Saf-T-Vu M1083 passing the KSC standard electrostatic test after treatment.

Optimization of air and oxygen plasma treatment was determined for all materials, confirmed by XPS that showed increased oxidation of the surface of all materials tested.

Further work to optimize modification for a more permanent effect by using different gases and exposure times will be undertaken.

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